



**WORLD INTELLECTUAL PROPERTY ORGANIZATION
ORGANISATION MONDIALE DE LA PROPRIÉTÉ INTELLECTUELLE**

34, chemin des Colombettes, Case postale 18, CH-1211 Genève 20 (Suisse)
Téléphone: (41 22) 338 91 11 - e-mail: wipo.mail @ wipo.int. - Fac-similé: (41 22) 733 54 28

**PATENT COOPERATION TREATY (PCT)
TRAITÉ DE COOPÉRATION EN MATIÈRE DE BREVETS (PCT)**

**CERTIFIED COPY OF THE INTERNATIONAL APPLICATION AS FILED
AND OF ANY CORRECTIONS THERETO**

**COPIE CERTIFIÉE CONFORME DE LA DEMANDE INTERNATIONALE, TELLE QU'ELLE
A ÉTÉ DÉPOSÉE, AINSI QUE DE TOUTES CORRECTIONS Y RELATIVES**

International Application No. }
Demande internationale n° } **PCT/IB02/00304**

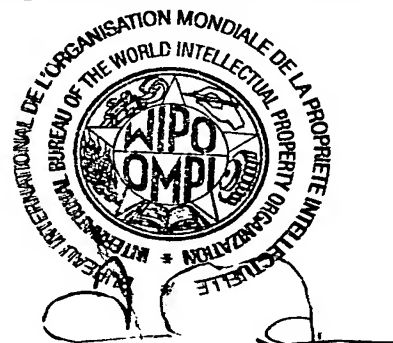
International Filing Date } **29 January 2002**
Date du dépôt international } **(29.01.02)**

Geneva/Genève,

**10 September 2003
(10.09.03)**

**International Bureau of the
World Intellectual Property Organization (WIPO)**

**Bureau International de l'Organisation Mondiale
de la Propriété Intellectuelle (OMPI)**



J.-L. Baron
Head, PCT Receiving Office Section
Chef de la section "office récepteur du PCT"

PCT REQUEST

5620-PCT

Original (for SUBMISSION) - printed on 29.01.2002 02:04:18 PM

0	For receiving Office use only	
0-1	International Application No.	PCT / IB 0 2 / 0 0 3 0 4
0-2	International Filing Date	2 9 JANUARY 2002 (2 9. 01. 02)
0-3	Name of receiving Office and "PCT International Application"	INTERNATIONAL BUREAU OF WIPO PCT International Application
0-4	Form - PCT/RO/101 PCT Request	
0-4-1	Prepared using	PCT-EASY Version 2.92 (updated 01.01.2002)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	International Bureau of the World Intellectual Property Organization (RO/IB)
0-7	Applicant's or agent's file reference	5620-PCT
I	Title of invention	A PROCESS FOR THE OXIDATION OF UNSATURATED ALCOHOLS
II	Applicant	
II-1	This person is:	applicant only
II-2	Applicant for	all designated States except US
II-4	Name	FIRMENICH SA
II-5	Address:	1, route des Jeunes P.O. Box 239 CH-1211 GENEVA 8 Switzerland
II-6	State of nationality	CH
II-7	State of residence	CH
II-8	Telephone No.	+41 22 780 22 11
II-9	Facsimile No.	+41 22 780 33 38
II-10	e-mail	annick.boccard@firmenich.com
III-1	Applicant and/or inventor	
III-1-1	This person is:	applicant and inventor
III-1-2	Applicant for	US only
III-1-4	Name (LAST, First)	WALTHER, Eric
III-1-5	Address:	14, rue Ecole-de-Médecine CH-1205 GENEVA Switzerland
III-1-6	State of nationality	CH
III-1-7	State of residence	CH

PCT REQUEST

5620-PCT

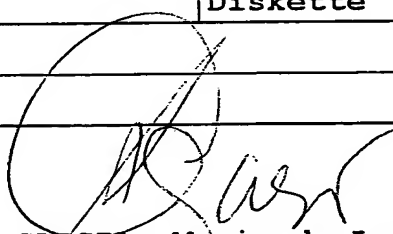
Original (for SUBMISSION) - printed on 29.01.2002 02:04:18 PM

IV-1	Agent or common representative ; r address for correspondence The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	agent
IV-1-1	Name (LAST, First)	SALVATERRA-GARCIA, Maria de Lurdes
IV-1-2	Address:	FIRMENICH SA P.O. Box 239 CH-1211 GENEVA 8 Switzerland
IV-1-3	Telephone No.	+41 22 780 22 11
IV-1-4	Facsimile No.	+41 22 780 33 38
V	Designation of States	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AP: GH GM KE LS MW MZ SD SL SZ TZ UG ZM ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE TR and any other State which is a Contracting State of the European Patent Convention and of the PCT OA: BF BJ CF CG CI CM GA GN GQ GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH&LI CN CO CR CU CZ DE DK DM DZ EC EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ OM PH PL PT RO RU SD SE SG SI SK SL TJ TM TN TR TT TZ UA UG US UZ VN YU ZA ZM ZW

PCT REQUEST

5620-PCT

Original (for SUBMISSION) - printed on 29.01.2002 02:04:18 PM

V-5	Precautionary Designation Statement In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.		
V-6	Exclusion(s) from precautionary designations	NONE	
VI	Priority claim	NONE	
VII-1	International Searching Authority Chosen	European Patent Office (EPO) (ISA/EP)	
VIII	Declarations	Number of declarations	
VIII-1	Declaration as to the identity of the inventor	-	
VIII-2	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	-	
VIII-3	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	-	
VIII-4	Declaration of inventorship (only for the purposes of the designation of the United States of America)	-	
VIII-5	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	-	
IX	Check list	number of sheets	electronic file(s) attached
IX-1	Request (including declaration sheets)	4	-
IX-2	Description	9	-
IX-3	Claims	4	-
IX-4	Abstract	1	EZABST00.TXT
IX-5	Drawings	0	-
IX-7	TOTAL	18	
	Accompanying items	paper document(s) attached	electronic file(s) attached
IX-8	Fee calculation sheet	✓	-
IX-17	PCT-EASY diskette	-	Diskette
IX-19	Figure of the drawings which should accompany the abstract		
IX-20	Language of filing of the international application	English	
X-1	Signature of applicant, agent or common representative		
X-1-1	Name (LAST, First)	SALVATERRA-GARCIA, Maria de Lurdes	

PCT REQUEST

5620-PCT

Original (for SUBMISSION) - printed on 29.01.2002 02:04:18 PM

FOR RECEIVING OFFICE USE ONLY

10-1	Date of actual receipt of the purported international application	29 JANUARY 2002 (29.01.02)
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/EP
10-6	Transmittal of search copy delayed until search fee is paid	✓

FOR INTERNATIONAL BUREAU USE ONLY

11-1	Date of receipt of the record copy by the International Bureau	
------	--	--

A PROCESS FOR THE OXIDATION OF UNSATURATED ALCOHOLS

Technical field

5

The present invention relates to the field of organic synthesis and more precisely to a process for the synthesis of an unsaturated aldehyde or ketone by oxidation of the corresponding alcohol. Said oxidation is characterized in that it is performed by a hypochlorite salt and a catalytic amount of a N-(2,2,6,6-tetraalkyl-4-piperidiny1-N-oxyl)-
10 2-amino-1,3,5-triazine derivative, preferably a N-oxyl derivative of the polymers known under the trademark Chimassorb® 944 or 2020 (origin: Ciba Specialty Chemicals, Basel, Switzerland).

15 Prior art

The oxidation of an alcohol into the corresponding aldehyde or ketone by a hypochlorite salt and in the presence of a N-oxyl derivative as catalyst is a very attractive process for the chemical industry as it involves cheap and readily available oxidant and
20 catalyst.

However, the prior art in this field proves that only saturated, benzylic or arylalkyl alcohols can be oxidized with good yield using such a process. Indeed, the use of unsaturated alcohols, e.g. having an alkenyl group, is quite rare and results always in very low yields, if none.

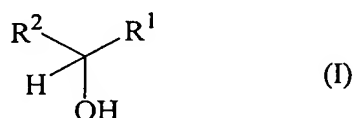
25

Description of the invention

In order to overcome the problems aforementioned, the present invention relates to
30 a catalytic process, with high yields, for the oxidation of unsaturated alcohols allowing the use of a hypochlorite compound as secondary oxidant.

The process of the invention concerns more specifically the oxidation of an unsaturated alcohol into the corresponding unsaturated aldehyde or ketone by means of a hypochlorite salt and a N-(2,2,6,6-tetraalkyl-4-piperidiny1-N-oxyl)-2-amino-1,3,5-triazine derivative as catalyst. By "unsaturated alcohol" it is meant an alcohol having one or more non-aromatic carbon-carbon double bond.

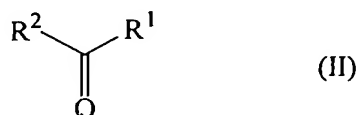
More precisely, the process of the invention concerns the oxidation of an unsaturated alcohol, or substrate, of formula



10

wherein R¹ represents a hydrogen atom, a C₁ to C₂₀ linear, branched or cyclic saturated or unsaturated hydrocarbon group, said hydrocarbon group being possibly substituted and also possibly comprising one or two oxygen or nitrogen atoms;

R² represents a C₂ to C₂₀ linear, branched or cyclic alkenyl, alkandienyl or alkantrienyl hydrocarbon group, said hydrocarbon group being possibly substituted and possibly comprising one or two oxygen or nitrogen atoms; or said R¹ and R² may be bonded together to form an unsaturated ring having 5 to 20 carbon atoms, said ring being possibly substituted and possibly comprising one or two oxygen or nitrogen atoms; and the possible substituents of R¹, R² and of the ring which said R¹ and R² may form together, are C₁ to C₁₅ linear, branched or cyclic alkyl, alkenyl or aromatic groups; into the corresponding unsaturated aldehyde or ketone of formula



wherein R¹ and R² are defined as in formula (I);

characterized in that said oxidation is performed by means of a hypochlorite salt of formula



in which M represents an alkaline metal, in which case n is 1, or an alkaline-earth metal in which case n is 2;

and of a catalytic amount of a N-(2,2,6,6-tetraalkyl-4-piperidiny-N-oxyl)-2-amino-1,3,5-triazine derivative.

5 As optional ingredient it may be added to the process of the invention a bromide salt of formula $M'Br$, wherein M' is an alkaline metal.

Preferred unsaturated alcohol, and the corresponding preferred unsaturated aldehyde or ketone, is a compound of formula (I), or (II) respectively, wherein R^1 represents a hydrogen atom;

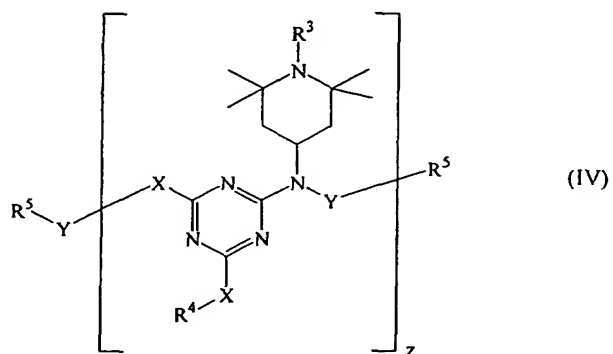
10 R^2 represents a C_5 to C_{15} linear, branched or cyclic alkenyl or alkandienyl hydrocarbon group, possibly substituted; or R^2 represents a C_7 to C_{15} linear, branched or cyclic alkantrienyl hydrocarbon group possibly substituted; and the possible substituents of R^2 are C_1 to C_8 linear, branched or cyclic alkyl, alkenyl or aromatic groups.

15 The hypochlorite salt is preferably selected in the group consisting of NaOCl, KOCl and $Ca(OCl)_2$.

Preferably, the bromide salt is KBr or NaBr.

The N-(2,2,6,6-tetraalkyl-4-piperidiny-N-oxyl)-2-amino-1,3,5-triazine derivative, the catalyst, is preferably a compound of formula

20



wherein z represents an integer from 1 to 20;

R^3 represents, simultaneously or independently, a hydrogen atom or an oxyl radical ($O\cdot$),

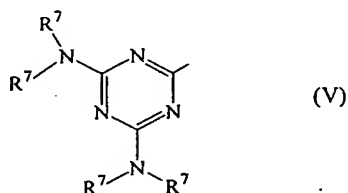
25 with the proviso that at least one R^3 group is an oxyl radical;

X represents an oxygen atom or a $-NR^4-$ group;

R^4 represents, simultaneously or independently, a hydrogen atom, a 2,2,6,6-tetramethyl-4-piperidiny group, a 2,2,6,6-tetramethyl-4-piperidiny-N-oxyl radical group or a C_1 to C_{15} linear, branched or cyclic saturated or unsaturated hydrocarbon group, said hydrocarbon group being possibly comprising one or two oxygen or nitrogen atoms; or two R^4 groups, bonded to the same nitrogen atom, may be bonded together to form a heterocycle having 5 to 7 members and which may contain an oxygen atom;

R^5 represents, simultaneously or independently, a hydrogen atom or a NR^6_2 group;

R^6 represents, simultaneously or independently, a hydrogen atom, a C_1 to C_{20} linear, branched or cyclic saturated or unsaturated hydrocarbon group, a 2,2,6,6-tetramethyl-4-piperidiny-N-oxyl radical group, a 2,2,6,6-tetramethyl-4-piperidiny group or a group of formula

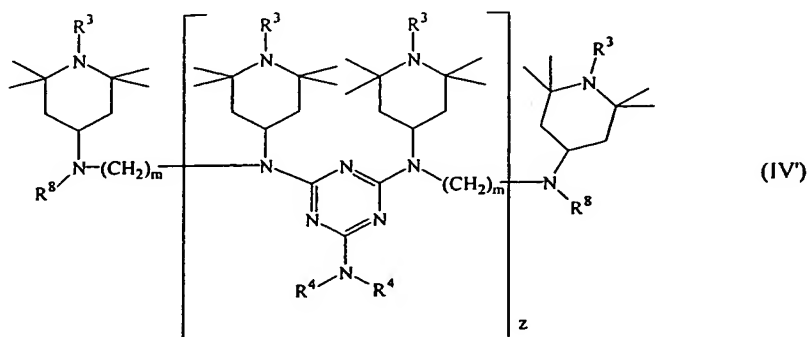


15

R^7 representing, simultaneously or independently, a hydrogen atom, a C_1 to C_{12} linear or branched alkyl group, a 2,2,6,6-tetramethyl-4-piperidiny-N-oxyl radical group or a 2,2,6,6-tetramethyl-4-piperidiny group; and

Y represents, simultaneously or independently, a C_2 to C_{20} linear, branched or cyclic alkylene group possibly comprising one or two oxygen or nitrogen atoms.

More preferably, the catalyst is a polymeric or oligomeric compound of formula



wherein z represents an integer from 2 to 10;

m represent an integer from 2 to 12;

R^3 is defined as for formula (IV);

R^4 represents, simultaneously or independently, a hydrogen atom, a 2,2,6,6-tetramethyl-4-piperidiny-N-oxyl radical group, a 2,2,6,6-tetramethyl-4-piperidiny group or a C_1 to C_{10} linear or branched alkyl or alkenyl group; or two R^4 groups, bonded to the same nitrogen atom, may be bonded together to form a heterocycle having 6 members and which may contain an oxygen atom; and

R^8 represents, simultaneously or independently, a hydrogen atom, a C_1 to C_{10} linear or branched alkyl or alkenyl group, a 2,2,6,6-tetramethyl-4-piperidiny-N-oxyl radical group, a 2,2,6,6-tetramethyl-4-piperidiny group or a group of formula (V) as defined previously.

Even more preferably, the catalyst is a N-oxyl derivative of the polymers having the CAS Registry Numbers 71878-19-8 or 192268-64-7 and which are also known under the trademark Chimassorb® 944 or 2020 respectively (origin: Ciba Specialty Chemicals, Basel, Switzerland). One of said derivatives of the Chimassorb® 944 is known in the literature with the name PIPO and has the CAS Registry Number 91993-31-6.

In a general way, the catalyst of formula (IV) can be prepared and isolated prior to its use according to the general methods described in the literature (E.G. Rozantsev *et al.* in Synthesis 1971, 190, or in the patent application FR 2788272).

Moreover, the catalyst of formula (IV) can be prepared *in situ*, by using the same methods mentioned herein above, in the reaction medium, without isolation or purification, just before their use.

The catalyst of formula (IV) can be added to the reaction medium in a large range of concentrations. As non-limiting examples, one can cite as catalyst concentration values those ranging from 0.02 to 0.15 molar equivalents, relative to the amount of alcohol of formula (I), preferably between 0.03 and 0.1 molar equivalents. It goes without saying that the optimum concentration of catalyst will depend on the nature of the latter and on the alcohol of formula (I) used during the process.

Concerning the quantities of the hypochlorite salt, which can be added to the reaction mixture, one can cite, as non-limiting examples, ranges between 0.9 and 1.5 molar equivalents, relative to the amount of alcohol of formula (I), preferably between 1.0

and 1.3 molar equivalents. Again the optimum concentration of hypochlorite salt will depend on the nature of the latter and on the alcohol of formula (I) used during the process.

The bromide salt MBr may be added in a quantity ranging between 0 and 0.05
5 molar equivalents relative to the amount of alcohol of formula (I), preferably between 0.005 and 0.015 molar equivalents.

The oxidation reaction can be carried out in the presence or absence of a solvent. When a solvent is required or used for practical reasons, then any solvent current in such oxidation reactions can be used for the purposes of the invention, provided that
10 the starting alcohol of formula (I) and the N-(2,2,6,6-tetraalkyl-4-piperidinyl-N-oxyl)-2-amino-1,3,5-triazine derivative are at least partially soluble. Non-limiting examples include aromatic solvents such as benzene, toluene or xylene, hydrocarbon solvents such as hexane or cyclohexane, dialkyl ethers such as methyl terbutyl ether, C₁ to C₆ alkyl acetate such an ethyl or propyl acetate, chlorinated solvents such as dichloromethane or
15 chloroform, or mixtures thereof. A person skilled in the art is well able to select the most convenient solvent in each case to optimize the oxidation reaction, however ethyl or propyl acetate, dichloromethane or toluene are the preferred solvents.

The temperature at which the process of the invention can be carried out is comprised between 0°C and 60°C, preferably in the range between 15°C and 40°C, more
20 preferably between 20°C and 25°C. Of course, a person skilled in the art is also able to select the preferred temperature as a function of the melting and boiling point of the starting and final products.

The invention will now be described in further detail by way of the following examples, wherein the abbreviations have the usual meaning in the art, the temperatures
25 are indicated in degrees centigrade (°C).

Example 1

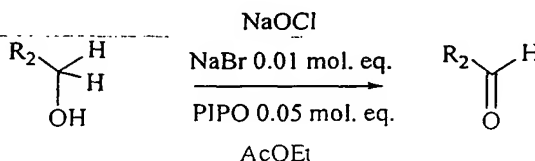
Oxidation of primary alcohols containing double bonds with NaOCl catalyzed by PIPO (N-oxyl derivative of Chimassorb® 944):

5

PIPO can be obtained according to any of the methods reported in the literature, e.g. the patent application FR 2788272 or Dijksman *et al.* in Synlett **2001**, 102-4.

General procedure:

10



In a 100 ml round bottomed flask were charged PIPO (0.05 molar equivalents) and NaBr (20% aqueous solution; 0.01 molar equivalents) followed by the alcohol to be oxidized (10 g, 1 molar equivalents) and ethylacetate as solvent (35 g). After dissolution of PIPO, it was introduced over one hour, at room temperature, an aqueous solution containing NaOCl (1.1-1.45 molar equivalents) and in which NaHCO₃ (2% weight/weight relative to NaOCl solution) was added just before use. At the end of the introduction, the stirring was continued for 15-45 min and afterwards the reaction mixture was allowed to stand until the phase separation. The aqueous phase was removed, and the organic phase was washed with water. Then, the organic phase was concentrated under vacuum and the clear orange crude product was purified by distillation (bulb-to-bulb) to afford the corresponding aldehyde. The aldehydes obtained had all the same spectroscopic data as reported in the literature.

The results obtained for the oxidation of some unsaturated alcohols are summarized in Table 1, herein below.

25

Table 1 : Results of the oxidation of some unsaturated alcohols into the corresponding aldehydes using NaOCl and PIPO as catalyst:

Alcohol ^{a)}	Aldehyde ^{a)}	Conversion of the alcohol (%)	Yield of the aldehyde (%)	NaOCl ^{b)}
1a	1b	99.5	90	1.05
1a ⁱ⁾	1b	79	20	1.25
2a	2b	100	99	1.05
3a	3b	97	70	1.45
4a ⁱⁱ⁾	4b	99	77	1.25
5a	5b	89	81	1.10
5a ⁱⁱⁱ⁾	5b	86	81	1.10
5a ^{iv)}	5b	55	-	1.10
6a	6b	98	82	1.18
7a	7b	90	77	1.30
7a ^{v)}	7b	5	-	1.30

5 a) alcohol or aldehyde of formula (II) or (I) respectively:

1a : 3-Phenyl-2-propen-1-ol

1b : 3-Phenyl-2-propenal

2a : (E)-2-Dodecen-1-ol

2b : (E)-2-Dodecenal

3a : 3,7-Dimethyl-2,6-octadien-1-ol

3b : 3,7-Dimethyl-2,6-octadienal

4a : (2E,4Z,7Z)-2,4,7-Decatrien-1-ol

4b : (2E,4Z,7Z)-2,4,7-Decatrienal

10 5a : (Z)-5-Octen-1-ol

5b : (Z)-5-Octenal

6a : 10-Undecen-1-ol

6b : 10-Undecenal

7a : 3-(4-Tert-butyl-1-cyclohexen-1-yl)-
1-propanol

7b : 3-(4-Tert-butyl-1-cyclohexen-1-yl)-
propanolal

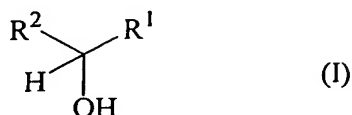
15 b) molar equivalent, relative to the amount of alcohol

- i) in CH_2Cl_2 , in the presence of 0.1 molar equivalent of KBr and with 0.01 molar equivalent of 4-methoxy-2,2,6,6-tetraalkyl-piperidine-N-oxyl (P. L. Anelli, C. Biffi, F. Montanari and S. Quici, *J. Org. Chem.* **1987**, 52, 2559).
- ii) in CH_2Cl_2 , with 0.1 molar equivalent of PIPO.
- 5 iii) in the absence of NaBr.
- iv) with 0.03 molar equivalent of 2,2,6,6-tetraalkyl-piperidine-N-oxyl.
- v) with 0.01-0.1 molar equivalent of 2,2,6,6-tetraalkyl-piperidine-N-oxyl.

Claims

1. A process for the oxidation of an unsaturated alcohol of formula

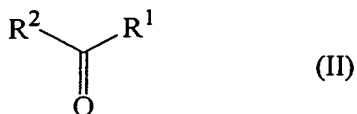
5



wherein R¹ represents a hydrogen atom, a C₁ to C₂₀ linear, branched or cyclic saturated or unsaturated hydrocarbon group, said hydrocarbon group being possibly substituted and also possibly comprising one or two oxygen or nitrogen atoms;

R² represents a C₂ to C₂₀ linear, branched or cyclic alkenyl, alkandienyl or alkantrienyl hydrocarbon group, said hydrocarbon group being possibly substituted and possibly comprising one or two oxygen or nitrogen atoms; or said R¹ and R² may be bonded together to form an unsaturated ring having 5 to 20 carbon atoms, said ring being possibly substituted and possibly comprising one or two oxygen or nitrogen atoms; and the possible substituents of R¹, R² and of the ring which said R¹ and R² may form together, are C₁ to C₁₅ linear, branched or cyclic alkyl, alkenyl or aromatic groups; into the corresponding unsaturated aldehyde or ketone of formula

20



wherein R¹ and R² are defined as in formula (I);

characterized in that said oxidation is performed by means of a hypochlorite salt of formula

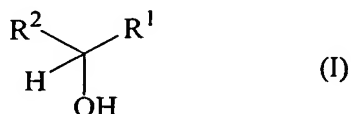
25



in which M represents an alkaline metal, in which case n is 1, or an alkaline-earth metal in which case n is 2;

and of a catalytic amount of a N-(2,2,6,6-tetraalkyl-4-piperidiny-N-oxyl)-2-amino-1,3,5-triazine derivative.

2. A process according to claim 1, characterized in that the unsaturated
5 alcohol is a compound of formula (I),

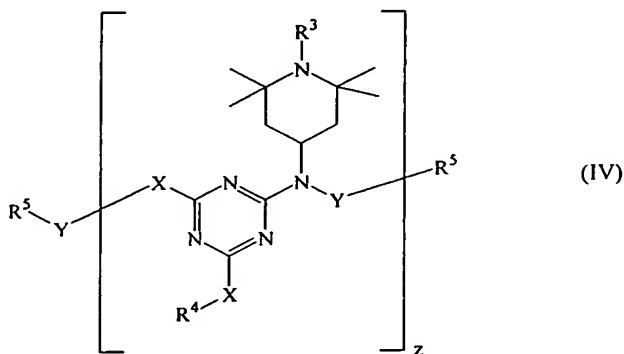


wherein R¹ represents a hydrogen atom;

- 10 R² represents a C₅ to C₁₅ linear, branched or cyclic alkenyl or alkandienyl hydrocarbon group, possibly substituted; or R² represents a C₇ to C₁₅ linear, branched or cyclic alkantrienyl hydrocarbon group possibly substituted; and
the possible substituents of R² are C₁ to C₈ linear, branched or cyclic alkyl, alkenyl or aromatic groups.

15

3. A process according to claim 1, characterized in that the N-(2,2,6,6-tetraalkyl-4-piperidiny-N-oxyl)-2-amino-1,3,5-triazine derivative is a compound of formula



20

wherein z represents an integer from 1 to 20;

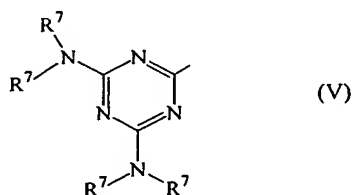
R³ represents, simultaneously or independently, a hydrogen atom or an oxyl radical (O[•]),
with the proviso that at least one R³ group is an oxyl radical;

X represents an oxygen atom or a $-NR^4$ - group;

R^4 represents, simultaneously or independently, a hydrogen atom, a 2,2,6,6-tetramethyl-4-piperidiny group, a 2,2,6,6-tetramethyl-4-piperidiny-N-oxyl radical group or a C_1 to C_{15} linear, branched or cyclic saturated or unsaturated hydrocarbon group, said hydrocarbon group being possibly comprising one or two oxygen or nitrogen atoms; or two R^4 groups, bonded to the same nitrogen atom, may be bonded together to form a heterocycle having 5 to 7 members and which may contain an oxygen atom;

R^5 represents, simultaneously or independently, a hydrogen atom or a NR^6_2 group;

R^6 represents, simultaneously or independently, a hydrogen atom, a C_1 to C_{20} linear, branched or cyclic saturated or unsaturated hydrocarbon group, a 2,2,6,6-tetramethyl-4-piperidiny-N-oxyl radical group, a 2,2,6,6-tetramethyl-4-piperidiny group or a group of formula



15

R^7 representing, simultaneously or independently, a hydrogen atom, a C_1 to C_{12} linear or branched alkyl group, a 2,2,6,6-tetramethyl-4-piperidiny-N-oxyl radical group or a 2,2,6,6-tetramethyl-4-piperidiny group; and

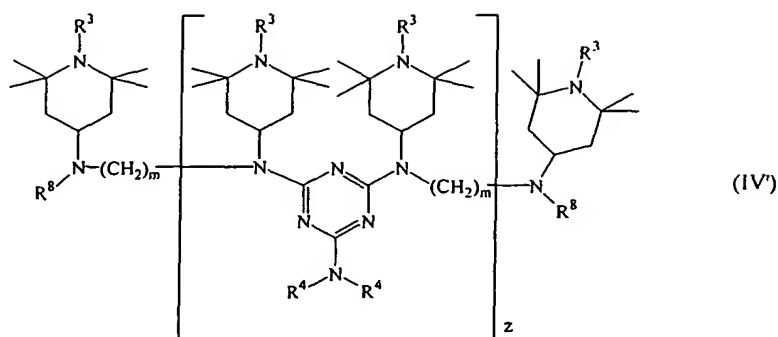
Y represents, simultaneously or independently, a C_2 to C_{20} linear, branched or cyclic alkylene group possibly comprising one or two oxygen or nitrogen atoms.

20

4. A process according to claim 3, characterized in that the N-(2,2,6,6-tetraalkyl-4-piperidiny-N-oxyl)-2-amino-1,3,5-triazine derivative is a polymeric or oligomeric compound of formula

25

13



wherein z represents an integer from 2 to 10;

m represent an integer from 2 to 12;

5 R^3 is defined as in claim 3;

R^4 represents, simultaneously or independently, a hydrogen atom, a 2,2,6,6-tetramethyl-4-piperidiny-N-oxyl radical group, a 2,2,6,6-tetramethyl-4-piperidiny group or a C_1 to C_{10} linear or branched alkyl or alkenyl group; or two R^4 groups, bonded to the same nitrogen atom, may be bonded together to form a heterocycle having 6 members and which may

10 contain a oxygen atom; and

R^8 represents, simultaneously or independently, a hydrogen atom, a C_1 to C_{10} linear or branched alkyl or alkenyl group, a 2,2,6,6-tetramethyl-4-piperidiny-N-oxyl radical group, a 2,2,6,6-tetramethyl-4-piperidiny group or a group of formula (V) as defined in claim 3.

15 5. A process according to claim 4, characterized in that the N-(2,2,6,6-tetraalkyl-4-piperidiny-N-oxyl)-2-amino-1,3,5-triazine derivative is a N-oxyl derivative of the polymers having the CAS Registry Numbers 71878-19-8 or 192268-64-7.

20 6. A process according to any one of claims 1 to 5, characterized in that the hypochlorite salt is selected in the group consisting of NaOCl, KOCl and $Ca(OCl)_2$.

7. A process according to any one of claims 1 to 6, characterized in that it is added to the process of the invention a bromide salt of formula $M'Br$, wherein M' is an alkaline metal.

25

8. A process according to claim 7, characterized in that the bromide salt is KBr or NaBr.

Abstract

5 The present invention relates to the field of organic synthesis and more precisely to a process for the synthesis of an unsaturated aldehyde or ketone by oxidation of the corresponding alcohol. Said oxidation is characterized in that it is performed by a hypochlorite salt and a catalytic amount of a N-(2,2,6,6-tetraalkyl-4-piperidiny1-N-oxyl)-2-amino-1,3,5-triazine derivative, preferably a N-oxyl derivative of the polymers known under the trademark Chimassorb® 944 or 2020.